

# Advances in the CIS Research at NREL

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## ADVANCES IN THE CIS RESEARCH AT NREL

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### ABSTRACT

This paper summarizes the research of the CIS Team at NREL in three major areas: absorber deposition; understanding the role of chemical bath deposited (CBD) CdS in CIS junctions; and in the development of devices without CdS. Low cost, scaleable processes chosen for absorber fabrication include sputtering, electrodeposition (ED), and close spaced sublimation (CSS). The interaction between the CBD and the CIS has been investigated and the results show that Cd might be instrumental in shaping the interface. We have also developed a process to fabricate a 13.5% efficiency ZnO/CuInGaSe<sub>2</sub> device without CdS or other buffer layers.

### INTRODUCTION

Thin film solar cells based on CuInSe<sub>2</sub> and its alloys with Ga and S have demonstrated excellent efficiencies. In our laboratory, a 17.7% efficiency device based on CuInGaSe<sub>2</sub>(CIGS) absorber was demonstrated [1]. We have thus far used physical vapor deposition (PVD) methods from elemental sources to understand the film growth, develop models and fabricate a variety of efficient devices [2,3]. PVD is an excellent tool for prototyping films in a small scale. It seems logical to extend the understanding gained from the PVD process to other deposition methods that are considered to be industrial processes. Furthermore, one can dissect the absorber fabrication into a few discrete steps as follows: precursor deposition, compound formation, recrystallization, and a final compositional tuning to terminate the absorber surface. The precursor serves as a template for subsequent reaction, and its deposition can be achieved at high rates and low temperatures through a variety of methods. Stacks of such layers can also be used. The three stage process [2] is a good example of this approach. The second step might involve a high temperature anneal in Se atmosphere. The final step may be accomplished by the addition of In and Ga selenides. Three precursor deposition processes were chosen as candidates for this study: electrodeposition, close spaced sublimation, and sputtering.

In the junction area, our objectives have been two fold. Under the auspices of the Thin Film Partnership Program, we have studied the role of chemical bath deposited (CBD) CdS and the CIGS. The wide spread use of CBD and its acceptance as the preferred junction

fabrication method must be contrasted with the poor knowledge of the interface created by it. The second goal is one of finding an alternative process for forming the junction which uses conventional techniques and environmentally benign chemicals.

### EXPERIMENTAL

The procedures for electrodeposition [4] and sputtering [5] have been described in previous publications and they will not be repeated here. The as deposited precursor films made by electrodeposition are a mixture of CIGS and Cu<sub>x</sub>Se phases, and they exhibit dense packing. The precursors are heated in a Se atmosphere to about 550°C to recrystallize the films. The film composition is adjusted by adding In and Ga. The sputtered precursors were deposited by d.c sputtering from a pressed target made up of a mixture of CIGS and Cu<sub>x</sub>Se. These films were again recrystallized at high temperatures in Se atmosphere. The CSS work was carried out in a reactor similar to the one used for CdTe depositions. Pre-synthesized In<sub>2</sub>Se<sub>3</sub> and Ga<sub>2</sub>Se<sub>3</sub> powders or crystallites were used as the sources. The source temperature was varied from 700°C to 750°C, and the substrate temperature was held between 550°C and 620°C. Evaporated Cu films, deposited on Mo/glass were used as the substrate. Argon or helium (5 Torr) was used as the background gas to establish the pressure regime. Baseline devices were fabricated with CdS/ZnO window layers. CdS was grown by the reaction of CdSO<sub>4</sub> and thiourea from an aqueous bath composed of 0.0015 M CdSO<sub>4</sub>, 1.5 M NH<sub>4</sub>OH and 0.15 M thiourea. Thiourea was added when the bath temperature was 40°C, and the reaction proceeded as the temperature rose to 72°C in about 5 min. This allowed the deposition of about 50 nm thick CdS layer.

For the junction studies, standard PVD grown CIGS films were used. To study the interaction of the chemical bath with the CIGS, partial electrolytes were used. For example, the effect of Cd alone was studied by treating the CIGS films in a bath containing CdSO<sub>4</sub>, NH<sub>4</sub>OH and water only (no thiourea), all other conditions being the same as the CBD CdS deposition. This is designated 'Cd PE' in the following sections. Photoluminescence emission (PLE) spectra were measured in a Nicolet FT-PL spectrometer using a diode laser excitation at 847 nm. The incident power was 0.73 mW, and the sample temperature was 86 K.

## RESULTS AND DISCUSSION

ED precursor films have proved to be well suited templates for further processing using the concept described before. Figure 1 shows the SEM images of a precursor film and a processed film. The precursor shows a compact, densely packed morphology. X-ray diffraction spectra show weak, and broad peaks corresponding to the chalcopyrite (112) and (204) planes.

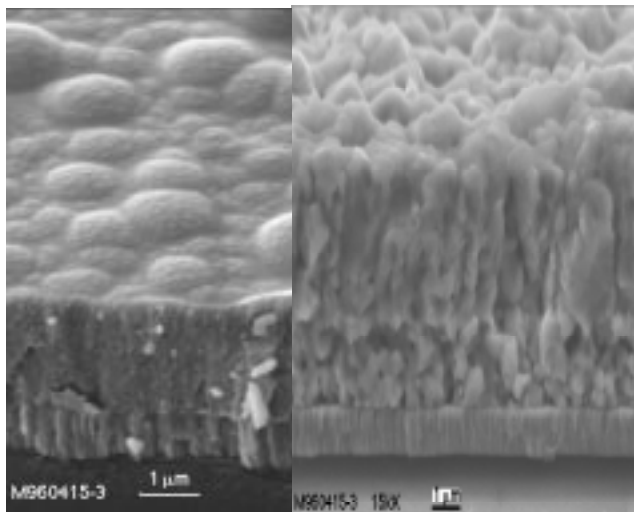


Fig 1. SEM images of ED precursor (left), and after recrystallization (right).

The appearance of the diffraction peaks for such a low temperature deposition is itself surprising, and this indicates microcrystalline character of the precursor films. The films are also very amenable to recrystallization at high temperatures and they do not exhibit the peeling and cracking encountered with Cu rich films prepared by other methods. A variety of absorbers have been prepared by the addition of In and Ga during the heat treatment. The Ga/(Ga+In) ratio has been varied from about 0.16 to 0.4, resulting in a wide range of band gaps. Open circuit voltages of up to 0.69 V have been already achieved, and even higher voltages should be possible. The efficiency of the devices range from 12.2% to 13.7% for the Ga contents specified above. The current-voltage curve for the highest efficiency device is shown in Fig. 2.

The ED precursors serve as a model from which we can learn how to process films obtained by other methods. When a similar approach is taken to recrystallize a sputtered precursor, the morphology of the final film shows a two layer structure where the recrystallization and densification occurs only in the upper part. This results in poor voltages and fill factors, limiting the efficiencies to about 8% at the present time.

The advantages of CSS as a manufacturing process for thin film CdS/CdTe PV devices are well known [6]. The suitability of CSS to CIS processing is not known, and we have made an attempt to study this. If  $\text{In}_2\text{Se}_3$  and

$\text{Ga}_2\text{Se}_3$  can be transported at appreciable rates using standard CSS methods, then one has to only contend with the delivery of Cu and the final reaction to form the compound. We found that  $\text{In}_2\text{Se}_3$  and  $\text{Ga}_2\text{Se}_3$  are well

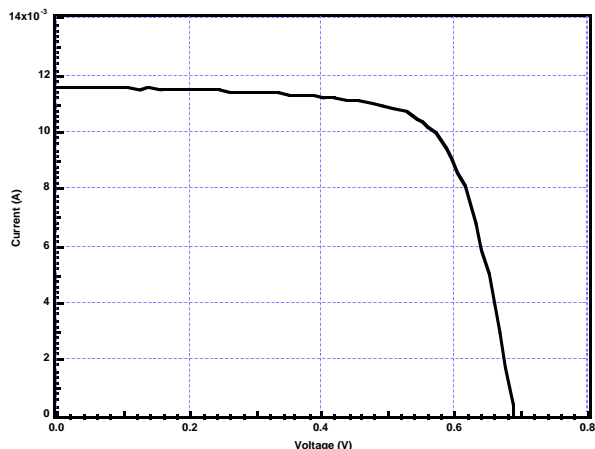


Fig. 2. Light I-V curve for a ZnO/CdS/CIGS device processed from ED precursor.

behaved sources, and thin films can be grown at the rate of about  $0.1 \mu\text{m}/\text{min}$  for a source temperature of  $750^\circ\text{C}$  and substrate temperature of  $600^\circ\text{C}$ , at an ambient pressure of 5 Torr He. Transport of  $\text{CuSe}$  or  $\text{Cu}_2\text{Se}$  was found to be problematic. The delivery of Cu was achieved by starting with a Cu film deposited on Mo/glass.  $\text{In}_2\text{Se}_3$ ,  $\text{Ga}_2\text{Se}_3$  and mixtures of the two were used as source materials and the films were deposited on Cu/Mo/glass substrates. The sublimation of  $\text{In}_2\text{Se}_3$  proceeds through a dissociation of

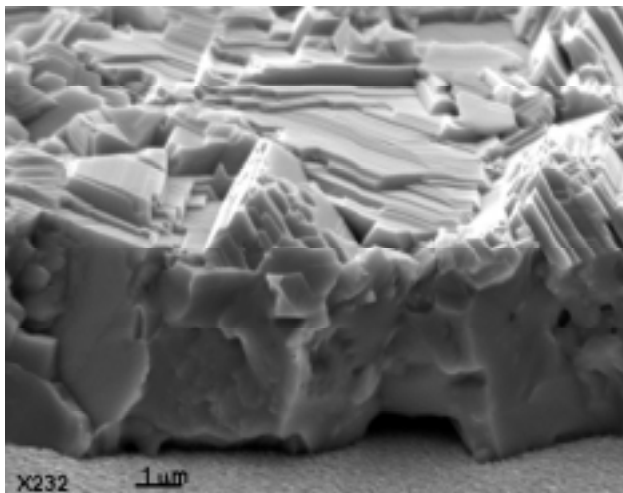


Fig. 3. SEM image of a CIS film made by CSS.

$\text{In}_2\text{Se}$  and  $\text{Se}_2$ . We found that the Cu reacted with the  $(\text{InGa})_x\text{Se}_y$  species, it was converted to CIS or CIGS when the deposition was conducted long enough for the reaction to go to completion (10 min). At shorter times, the films were found to be a mixture of  $\text{Cl(G)S}$  and  $\text{Cu}_x\text{Se}$ . The SEM image of a CIS film by this method is shown in Fig. 3. Growth from a Cu rich front results in excellent

morphology. The Se supply, obtained during the dissociation of  $\text{In}_2\text{Se}_3$  appears to be sufficient to selenize the films. This work is in its early stages. Device efficiencies are limited to 5% at this time. However, 13-14% devices could be made from absorbers fabricated by simulating the experiment in the coevaporation mode.

#### CBD CdS/CIS Interface

We consider the interaction between the chemical bath process and the CIGS films. Treatments in partial electrolyte solutions were conducted to separate out the effects of Cd, S and CdS. Figure 4 shows the I-V characteristics of five devices fabricated from identical CIGS films. When ZnO is sputtered directly (open circles) or when PVD CdS is used as the buffer layer (triangles), very poor characteristics are obtained. When the CIGS films are treated in Cd PE before such depositions are

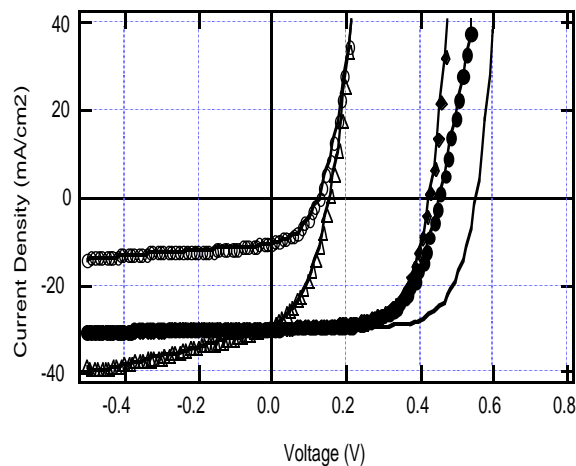


Fig. 4. Light I-V curves for CIGS films with various treatments.

made, a significant improvement occurs (diamonds and solid circles, respectively), and the device performance approaches that of the control device made with CBD CdS/ZnO window layers (solid line). It is clear that the Cd PE treatment modifies the CIGS surface favorably as evidenced by the increases in  $V_{oc}$ ,  $J_{sc}$  and fill factor. Chemical composition of the CIGS films was determined using X-ray photoelectron spectroscopy before and after the Cd PE treatment. About 20 at.% Cd was detected, and it was found to trail off to a much lower value at a depth of 5-10 nm. The introduction of Cd can easily occur in the CIS. The Cu deficient nature of the surface makes for an ideal route for substituting Cd in the Cu vacancy sites. In fact, the ionic radius of  $\text{Cd}^{2+}$  is 0.97 Å and that of  $\text{Cu}^+$  is 0.96 Å.

Fig. 5. shows the PL emission spectra obtained at 86 K for a set of identical CIGS samples treated with Cd PE and CdS. The excitation wavelength is well above the gap, and it is expected to be very strongly absorbed in the first 0.5  $\mu\text{m}$  of the CIGS. For the CdS coated CIGS, the emission originates from the CIGS because CdS does not

contribute to the emission. The spectrum for the CIGS sample heated in  $\text{NH}_4\text{OH}$  only (baseline reference) shows two principal emission peaks centered around 0.97 eV and 1.05 eV. These transitions have been ascribed to donor-to-acceptor (DA) pair transitions, involving two donor levels and one acceptor level (7). A major change of the emissions is observed after the Cd PE treatment. The highest energy peak at 1.05 eV is almost quenched, and the 0.97 eV emission is enhanced. There is now a new emission at 0.91 eV which is stronger than the others. The most striking feature of the spectra is the similarity of the emissions for the CIGS treated in Cd PE and the CIGS coated with CdS, and this leads us to speculate that the Cd influence is the key part of the CBD process. The intensity of the peaks increase by a factor of five after the CdS covered CIGS is annealed in air at 200°C for 2 min. This could be interpreted as a better passivation of the interface; typically such an anneal yields better voltages and fill factors.

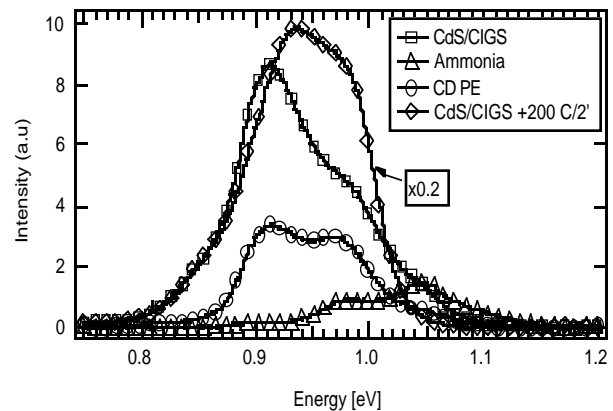


Fig. 5. PL spectra of CIGS films after various chemical treatments.

The quenching of the highest energy emission can be interpreted to be due to a reduction of the shallowest acceptor levels in the CIGS. If we assume that the action of  $\text{Cd}^{2+}$  ions on Cu vacancies (arguably the shallowest acceptor) produces substitutional donors, we expect the DA emission to decrease due to a reduction of the shallow acceptor levels. This argument is also consistent with the hypothesis of a type conversion, where the conductivity of a mildly n-type, Cu deficient surface region (OVC) is now enhanced by Cd doping. The appearance of the 0.91 eV peak can be due to a new DA pair, the origin of which is not possible to determine at this stage. It is possible that Cd introduces a new donor level (deeper). The above observations lead us to argue that the effect of CBD process are two fold. In the first phase, the Cd substituted CIGS is formed, resulting in an n type region. The downshift of the spectra by approximately 0.15 eV suggests that the formation of a different phase or alloy region can not be ruled out. The formation of an intermediate, alloyed region such as  $\text{CdSe}$  or  $\text{CdIn}_2\text{Se}_4$  has been suggested [8] and we consider it very likely. In the

second phase of the CBD, the CdS film grows slowly as the sulfur is slowly released by the hydrolysis of thiourea. The CdS layer can be viewed as a "buffer", and it provides a transition region as well as some shielding against sputter damage during the ZnO deposition.

#### Alternative Junction Fabrication Process

Insight and understanding gained from the studies described in the previous section were used to develop a set of criteria for forming junctions without Cd, CdS or other extrinsic "buffer layers". The eventual goal is to demonstrate an in-line process step that follows the absorber deposition in a seamless manner. Wet chemical steps are not favored, and the process should be capable of rapid throughput. Atmospheric pressure or moderate vacuum conditions are preferred. Environmental concerns preclude the use of Cd and other heavy elements. Finally, the devices should not require a heat treatment or light soaking, and they must show good stability under light exposure and moderate heating.

We have developed a method for fabricating CIS junctions which does not involve the use of Cd or other buffer layers. The details are the subject of a patent

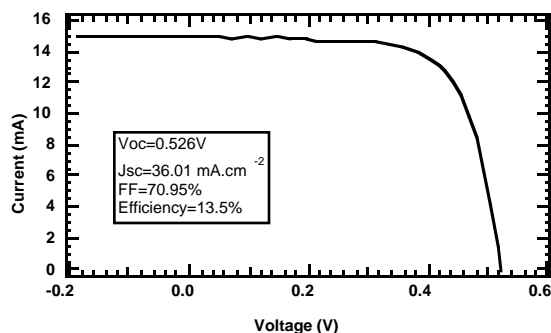


Fig. 6. Light I-V curve for a CdS free  $\text{MgF}_2/\text{ZnO}/\text{CIGS}$  device. Measured at NREL XT 25 solar simulator.

application. The CIGS bulk and surface compositions are found to be the important factors. At present, the junction formation is carried out *ex situ*, and in-line processing is being investigated. Following the junction formation step, a standard bilayer ZnO is deposited by r.f. sputtering in the usual manner. It must be pointed out that direct sputtering of the ZnO on CIGS typically yields only 2-5% devices. Fig. 6 shows the I-V characteristics of the best device obtained so far. The device efficiency is 13.5% and it is somewhat limited by the low Ga content of the absorber. The performance of the device is comparable or slightly better than the control device with CdS/ZnO window layers, fabricated on another part of the same absorber. The current density is higher in the buffer free device because of the elimination of CdS related absorption losses. The device parameters did not show any degradation due to light soaking or short anneals at 200°C. A slight improvement in  $V_{oc}$  and fill factors were noted. We believe that the junction formation can be

accomplished *in situ* or *ex situ* using established techniques employed in other semiconductor industries.

## CONCLUSIONS

In this report, we have summarized our work in the absorber deposition and junction formation. The role of CBD CdS in the CIS junctions was studied carefully using PL. The results show that Cd doping of the CIS might be an important first step in the junction formation. We have also developed a method for fabricating efficient devices that do not contain CdS or other buffer layers.

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